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THE SECONDARY PRECIPITATION OF GOLD IN ORE BODIES

A DISSERTATION
SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL OF
SCIENCE IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(DEPARTMENT OF GEOLOGY)

BY
ALBERT DUDLEY BROKAW

Reprinted from
THE JOURNAL OF GEOLOGY, Vol. XXI, No. 3
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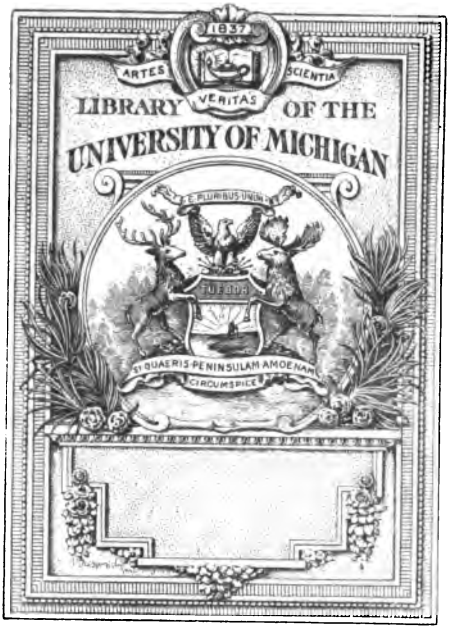
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THE SECONDARY PRECIPITATION OF GOLD IN ORE BODIES

ALBERT D. BROKAW
University of Chicago

Secondary enrichment of ore deposits has been recognized as a subject of fundamental importance to the economic geologist, and in recent years has received considerable study, both in the field and in the laboratory. The chemical reactions involved are, in many cases, less complex and more readily susceptible to laboratory study than many of the other great problems of earth chemistry. The temperatures, pressures, and concentrations involved are well within the range easily obtainable in the laboratory; the reacting substances are less numerous, and their chemistry is better understood than is the case with the substances and reactions involved in petrogenesis.

In December, 1909, Emmons[1] published a paper calling attention to the relationship between placer deposits and manganiferous and manganese-free gold ores, suggesting manganese as a determining factor in the solution of gold. About the same time the writer began a series of experiments dealing with the solution of gold in secondary enrichment, the results of which were published in May 1910.[2] In October, 1910, Emmons published a somewhat comprehensive review of the chemical and geological data available, with special reference to the gold deposits of the United States.[3] Very little material bearing on the subject has appeared since that time, and at the suggestion of Dr. Emmons the writer undertook a series of experiments with the hope of clearing up some important points in connection with the chemistry of the precipitation of gold, and in particular, of establishing the peculiar set of conditions under which gold and manganese dioxide may be precipitated

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[1] W. H. Emmons, *Min. and Sci. Press*, XCIX, 751–54, and 782–87 (1909).

[2] A. D. Brokaw, *Jour. Geol.*, XVIII, 321–26 (1910).

[3] W. H. Emmons, *Trans. Am. Inst. Min. Eng.*, XLII, 1–73 (1911).

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simultaneously, since manganese dioxide has been considered favorable, if not essential, to the solution of gold in secondary enrichment.

The methods of precipitation here discussed are not necessarily limited to secondary enrichment. Gold from a primary deposit may be recrystallized; that is, may be dissolved and reprecipitated without appreciable transportation, and in this case no enrichment would be accomplished, though the chemistry of the precipitation might be essentially the same as that in which gold deposits are enriched. For this reason the writer does not hesitate to draw examples from deposits where the gold has been recrystallized by secondary processes even though the deposit is not thought to have undergone any appreciable enrichment.

The substances in an ore body, capable of precipitating gold from a solution in which it is held as a chloride, may be grouped as follows:

I. Native elements, copper, silver, mercury, tellurium.
II. Sulphides, tellurides, etc.
  a) Simple—most of the common sulphides.
  b) Complex—sulph-arsenides and antimonides.
III. Ferrous compounds.
  a) In solution derived from alteration of iron sulphides.
  b) Primary minerals, as siderite, iron bearing calcite, etc.
IV. Manganous compounds.
  a) In solution, derived from alteration of manganese minerals.
  b) Primary, rhodochrosite.
V. Other inorganic substances, sulphur dioxide.
VI. Organic compounds.

I. NATIVE ELEMENTS

The metals preceding gold in the table of electrolytic solution tension[1] are capable of displacing it from solutions of its salts. The reaction may be expressed ionically as follows:

$$Au^{+++} + 3Me = Au + 3Me^{+}$$

in which Me stands for one equivalent weight of the metal in question. Copper and silver are not uncommon in gold deposits and are capable of bringing about such precipitation. Doubtless native mercury, arsenic, and antimony can act in a similar way. There is, however, little geological evidence of such precipitation, though it is conceivable that electrum may sometimes be formed in this way. Ransome[1] mentions the association of wire gold with native silver in the Breckenridge district, and here the silver may have been the precipitating agent. The other metals having a higher electrolytic solution tension than gold and occurring free in nature are not common in gold deposits, and no record of their having caused precipitation of gold is found. Tellurium, usually classed as a non-metal, may interact with gold chloride in solution to precipitate gold, as shown by the following equation:[2]

---

[1] See Smith, *General Inorganic Chemistry*, p. 670; Walker, *Introduction to Physical Chemistry*, or any textbook of physical chemistry.

$$3Te+4AuCl_3=4Au+3TeCl_4$$

This may account, in part, for the precipitation of gold in the oxidized portion of gold telluride deposits.

II. SULPHIDES, TELLURIDES, ETC.

a) *Simple sulphides.*—That sulphides are capable of precipitating gold has been known for many years. In 1866 Wilkinson[3] showed that metallic gold is precipitated by the sulphides of copper, iron, arsenic, lead, zinc, molybdenum and tungsten, and to this list Skey[4] added the sulphides of tin, bismuth, platinum and gold. These investigators showed that the precipitates obtained were metallic gold, not gold sulphide, though the latter would be the compound naturally expected by some such reaction as follows:

$$2AuCl_3+3ZnS=Au_2S_3+3ZnCl_2$$

It is of interest to consider the possible reasons for the precipitation of the metal instead of the sulphide.

Hydrogen sulphide, under ordinary conditions of temperature and pressure in the laboratory, reacts with gold salts in solution to form Au_2S_2,[5] a stable sulphide of extremely low solubility, as follows:

$$8AuCl_3+9H_2S+4H_2O=4Au_2S_2+24HCl+H_2SO_4$$

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[1] F. L. Ransome, *U.S. Geol. Survey, Professional Paper No. 75*, p. 82.

[2] V. Lenher, *Jour. Am. Chem. Soc.*, XXIV, 355 (1902).

[3] *Trans. Roy. Soc., N.S.W.*, VIII, 11 (1866).

[4] *Chem. News*, XXIII, 232; see *J. B. u. d. Fortschritte d. Ch.*, 1871, p. 344.

[5] Gmelin-Kraut, V, P. II, p. 268.

Hydrogen sulphide may be formed by the interaction of acid mine waters on mineral sulphides, for example, on zinc blende, as follows:

$$H_2SO_4+ZnS=H_2S+ZnSO_4$$

This reagent is doubtless an important precipitant for gold in such waters. Why then, does it throw down metallic gold in nature, instead of gold sulphide, as in the laboratory?

A number of factors may be mentioned as probable causes. Hydrogen sulphide is given off very slowly by most of the mineral sulphides except pyrrhotite and zinc blende, even in fairly strongly acid solutions. It has been shown that in the presence of auric chloride, gold sulphide is oxidized to metallic gold and sulphuric acid, with the further precipitation of gold from the solution,[1] probably according to the equation:

$$Au_2S_2+4AuCl_3+8H_2O=6Au+2H_2SO_4+12HCl$$

Since the hydrogen sulphide is very slowly evolved, it may be that the gold sulphide is momentarily formed and immediately oxidized by the adjacent gold chloride molecules, which have not yet been attacked by the hydrogen sulphide. The reaction was tested experimentally by placing in a dilute solution of gold chloride fragments of pyrrhotite and zinc blende, the mineral sulphides which give off hydrogen sulphide the most readily and are therefore the most favorable for the precipitation of gold sulphide. In the case of zinc blende the surface of the crystal was covered with shining flakes of gold after standing 24 days. No gold sulphide could be distinguished. In the case of pyrrhotite the action was more rapid and the gold was completely precipitated in 3 days, but here again no gold sulphide was detected. The pyrrhotite was covered with a dull yellowish-brown coat, which, under the microscope was shown to be made up of minute crystals of gold, partly imbedded in material resembling limonite.

A second possibility is that ferric salts may oxidize the gold sulphide in a similar fashion. With this in mind, a solution of gold chloride and ferric sulphate was treated with hydrogen sulphide solution until a dark precipitate began to form. A small amount of sulphuric acid was added to suppress the precipitation of ferrous sulphide. The solution and precipitate were allowed to stand over night, then filtered, and the precipitate was taken into solution with fuming nitric acid and a small amount of concentrated hydrochloric acid. If any sulphide were present it would be oxidized to sulphate under these conditions. The solution was diluted and filtered; barium chloride solution gave no precipitate, showing the absence of sulphates, and thus proving that no gold sulphide was present in the precipitate. It is conceivable under these conditions that the hydrogen sulphide may have reduced some of the ferric salt before the gold began to precipitate and that the ferrous salt precipitated the gold. If this had been the case the precipitate should have shown the presence of sulphur, according to the reaction:

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[1] Gmelin-Kraut, *loc. cit.*

$$Fe_2(SO_4)_3+H_2S=2FeSO_4+H_2SO_4+S$$

which takes place before the precipitation of ferrous sulphide begins. The action of the nitric acid in the above experiment would have oxidized such precipitated sulphur to sulphuric acid, and as the test showed the absence of sulphates it is evident that the above reaction did not take place, but that the hydrogen sulphide acted on the gold chloride. The gold sulphide, Au_2S_2, was probably formed first, then quickly oxidized to metallic gold ? and sulphuric acid by the ferric sulphate present.

A further experiment along the same line was made as follows: Gold sulphide was precipitated and placed in contact with ferric sulphate, free from ferrous salt. After two weeks the solution contained a noticeable amount of ferrous salt, showing that part of the ferric salt had been reduced by the gold sulphide, but the appearance of the precipitate had not changed appreciably. Fresh ferric salt solution was added with similar results, and after standing three months small particles of what appeared to be gold could be seen. They could not be separated from the gold sulphide however, and the evidence that they were particles of gold is far from conclusive.

From these experiments it seems likely that the presence of ferric salts tends to cause the precipitation of free gold rather than gold sulphide, in the presence of hydrogen sulphide and sulphuric acid. Equations may be written as follows:

$$8AuCl_3+9H_2S+4H_2O=4Au_2S_2+24HCl+H_2SO_4$$

$$Au_2S_2+6Fe_2(SO_4)_3+8H_2O=2Au+12FeSO_4+8H_2SO_4$$?

These reactions may help explain the fact that, so far as we know, gold sulphide does not occur in nature.

A number of natural tellurides, including all the commoner telluride ores, have been shown to react with gold chloride in a manner similar to that of free tellurium,[1] for example:

$$3Au_2Te+4AuCl_3=10Au+3TeCl_4$$

and as is the case with tellurium, this may help to account for the free gold in the oxidized portion of the ore body, such as the "rusty gold" or "flour gold" at Cripple Creek.

b) *Complex sulphides.*—From the fact that most of the simple sulphides precipitate gold from solution it is readily inferred that complex sulphides would be equally effective as precipitants. Polybasite was chosen for an experiment on this point. A small fragment of a good crystal of polybasite (Ag_9SbS_6) was placed in 5 c.c. of gold chloride solution containing 0.5 per cent gold. After 10 days the gold had been completely precipitated, forming a dull coat over the crystal, resembling that formed on pyrrhotite. Doubtless many of the complex sulphides would react in a similar manner, though geological observations bearing on such precipitations are lacking. Perhaps this is because the complex sulphide, after precipitating gold, has been more or less completely removed by oxidation.

III. FERROUS COMPOUNDS

a) *In solution.*—The fact that ferrous salts can precipitate gold from solutions of its salts has long been known. The reaction is ordinarily written:

$$3FeSO_4+AuCl_3=Au+Fe_2(SO_4)_3+FeCl_3,$$

or ionically,

$$3Fe^{++}+Au^{+++}=3Fe^{+++}+Au$$

This reaction was formerly used in metallurgical practice, but recently has been largely displaced by other methods. The most abundant source of ferrous sulphate in mine waters is found in the iron sulphides, which, upon partial oxidation, give rise to ferrous sulphate and sulphuric acid. These are almost always present in the zone where the sulphides are undergoing oxidation, and, because of the downward movement of the waters, and the presence of reducing agents lower down, ferrous salts are likely to be abundant below this zone. In such an ore body gold cannot migrate far, since ferrous salts, even in small amounts, almost prohibit the transportation of gold in solution.[1] Ferrous salts in solution are more abundant in mine waters than is hydrogen sulphide, and are doubtless a more important factor in the secondary precipitation of gold.

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[1] V. Lenher, *op. cit.*

McCaughey[2] showed the effect of ferrous salts on the solubility of gold in concentrated solutions of ferric salts, and doubtless an equilibrium condition exists between the concentrations of ferrous, ferric, and gold salts in solution, in contact with metallic gold. The equation may be written in the ionic form:

$$3Fe^{+++} + Au = 3Fe^{++} + Au^{+++}$$

whence the equilibrium equation:

$$\frac{[Fe^{++}]^3 \times [Au^{+++}]}{[Fe^{+++}]^3} = K$$

McCaughey's results were not sufficient to give the value of this constant, but more complete experiments would doubtless show such a relationship—indeed the form of curve obtained shows qualitatively that some such relationship exists.

If the condition of equilibrium were satisfied, fluorite may disturb it by going into solution and giving rise to the fluoride ion, which forms a little dissociated complex with the ferric ion,[3] practically removing it from the system and allowing the ferrous ion to cause precipitation. This case, though theoretically possible, is probably not of great importance in nature on account of the very low solubility of gold in ferric salts at concentrations obtaining in mine waters.

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[1] McCaughey, *Jour. Am. Chem. Soc.*, XXXI, 1261 (1909). See also Emmons, *loc. cit.*

[2] *Loc. cit.*

[3] Stieglitz, *Qualitative Analysis*, Part I, 271 (New York, 1912).

b) ***Primary iron minerals other than sulphides.***—Siderite is capable of precipitating gold from solution as follows:

$$AuCl_3+3FeCO_3+3H_2O=Au+3CO_2+FeCl_3+2Fe(OH)_3$$

Of this reaction we have geological evidence in the form of gold pseudomorphs after siderite, in which gold gives a sort of skeleton of the siderite replaced, since its volume is less than that of the siderite.

The specimen shown in Figs. 1, 2, and 3 is from the collection in Walker Museum, University of Chicago. The precipitation of gold by means of siderite was easily accomplished in the laboratory. A cleavage block of light-colored siderite was placed in 10 c.c. of 0.5 per cent gold solution, and after two weeks flakes of gold could be distinguished on the faces of the mineral. In another experiment sulphuric acid was added to the gold chloride solution. In this case the precipitation was more rapid, the siderite being nearly covered with shining flakes of gold after four days. After two weeks typical "wire gold" was noted, more or less coated with limonite. It is worthy of note that many occurrences of wire gold are found imbedded in a gangue of limonite. Ransome,[1] in describing specimens of gold from the Breckenridge district in

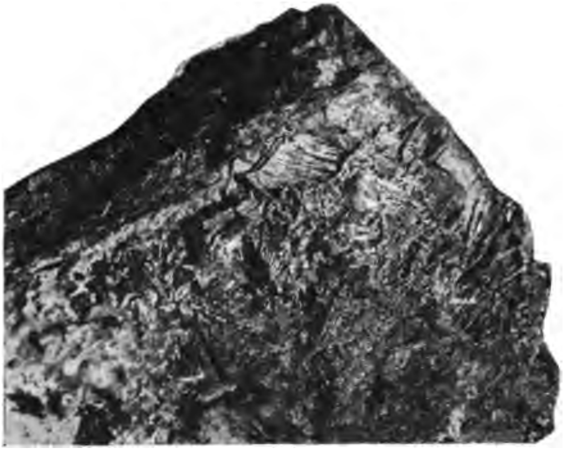

FIG. 1.—Gold replacing iron carbonate. × 2

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[1] F. L. Ransome, *U. S. Geol. Survey, Professional Paper No. 75*, pp. 81–82.

Colorado says, "The leaf gold is in exceedingly irregular masses, many of which consist of thin septa meeting at angles that strongly suggest deposition controlled in part by the cleavage planes of a rhombohedral carbonate of the calcite group. . . . . The [wire] gold does not occur in the clean, bright condition familiar in cabinet specimens, but is imbedded in a reddish, earthy matrix, consisting largely of limonite, with oxides and carbonates of copper and various earthy impurities."

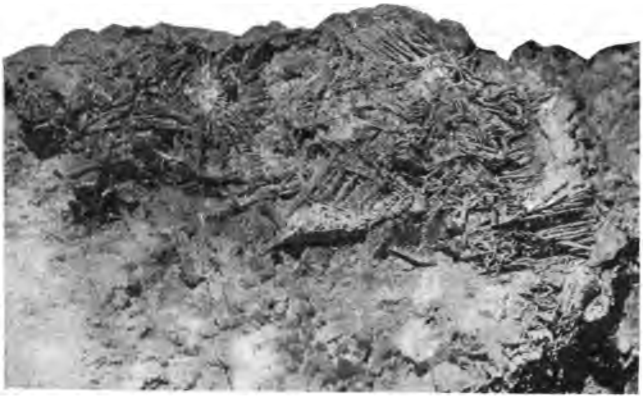

FIG. 2.—Gold replacing iron carbonate. × 2

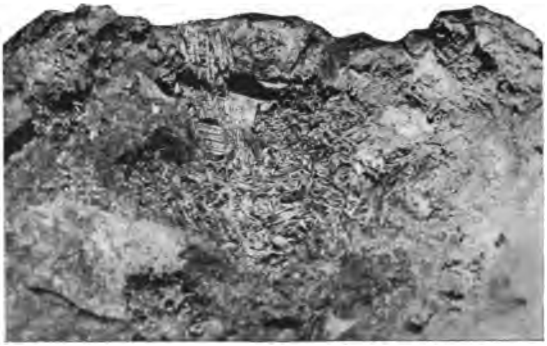

FIG. 3.—Gold replacing iron carbonate. × 2

No doubt iron-bearing calcite can cause a similar precipitation, providing the iron is in the ferrous state of oxidation. Calcite is, of course, much more abundant than siderite in most gold deposits. Analyses of calcite often show small amounts of ferrous carbonate, ranging in some cases up to 6 per cent. In sixteen analyses reported by Doelter[1] only three showed no ferrous iron, and the average for the sixteen was 1.33 per cent, reported as FeO.

Magnetite and olivine were selected as fairly simple ferrous compounds, and were allowed to stand in contact with a 0.5 per cent gold solution for 60 days. Neither one showed any precipitation of gold.

IV. MANGANOUS COMPOUNDS

a) *Manganous salts in solution.*—The fact that manganous salts, under certain conditions, can precipitate gold from solution and at the same time be oxidized to the insoluble manganese dioxide, seems to have escaped the attention of chemists. At least the writer has searched through chemical literature in vain for information on the subject. Wells[2] has called attention to the increased ease of oxidation of manganous salts in alkaline solutions, but the application to precipitation of gold has not been made.

The interesting occurrences of gold and manganese dioxide in a number of localities, notably in the San Juan,[3] Crede,[4] Park City[5] and Red Cliff[6] led to the suspicion that under the proper conditions manganous salts might act as the precipitating agent according to some such reaction as the following:

$$2AuCl_3+3MnSO_4+12H_2O=2Au+3MnO_2+6HCl+3H_2SO_4$$

Since this is the reverse of the reaction believed to be responsible for the solution of gold in the surface alteration of ore bodies, it is to be expected that it proceeds in this direction only under certain conditions, and the following series of experiments was undertaken with a view to ascertaining these conditions.

Gold chloride solutions of varying concentration were mixed with manganous sulphate solutions with concentrations ranging from normal up to saturation, but no precipitation occurred, even when the solutions were boiled for several minutes. All of these solutions gave acid reaction, due partly to the hydrolysis of the auric chloride:

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[1] C. Doelter, *Handbuch der Mineral-Chemie*, I, 274–75. (Dresden, 1911.)

[2] Cited by W. H. Emmons, *Trans. Am. Inst. Min. Eng.*, XLII, 29 (1911).

[3] Ransome, *U.S. Geol. Survey, Bull. No. 182*, p. 101 (see also Emmons, *op. cit.*, 31).

[4] Emmons and Larsen, *U.S. Geol. Survey, Bull. No. 530.*

[5] *U.S. Geol. Survey, Professional Paper No. 77*, p. 103.

[6] S. F. Emmons, cited by W. H. Emmons, *op. cit.*

$$AuCl_3+3H_2O=Au(OH)_3+3HCl$$

and partly to the addition product of auric chloride and water, H_2AuCl_3O, which ionizes as an acid[1] as follows:

$$H_2AuCl_3O=2H^{+}+AuCl_3O^{=}$$

It is well known that the efficacy of many reducing agents is increased by the alkalinity as is readily explained by the electrolytic theory of oxidation and reduction.[2] In accordance with this theory it was thought that neutralization of the acid solution might induce precipitation. N/50 potassium hydroxide was slowly added to 10 c.c. of a solution N/5 with respect to manganous salt and containing 75 mg. of gold as chloride. When about 6 c.c. had been added a brown precipitate began to form. The alkali was added until the solution was nearly neutral with respect to litmus, the precipitate was collected on a filter, and the manganese oxide was removed by digesting with a mixture of oxalic and sulphuric acids of known reducing strength. The residue was brought into a crucible, dried, and shown to be metallic Au.

In order to determine which oxide of manganese was formed in this reaction, the solution in the oxalic and sulphuric acid was divided into two equal parts. One of these was analyzed for manganese, and the other titrated with standard potassium permanganate solution to ascertain the loss of oxalic acid due to oxidation by the manganese oxide. The titration showed an oxidation of oxalic acid corresponding to one atom of oxygen for every molecule of MnO as determined in the analysis for manganese. The precipitate was clearly MnO_2, doubtless with water of hydration. In a check experiment the manganese oxide was taken into solution with a mixture of oxalic and sulphuric acids, equivalent to 45.28 c.c. N/10 alkali. After dissolving the precipitate the solution was equivalent to 32.26 c.c. N/10 alkali, having lost the equivalent of 11.02 N/10 acid. The manganese in solution was then converted to manganese dioxide by a standard method[1] and redissolved in the standard mixture of oxalic and sulphuric acids. Essentially the same loss of acid was obtained (10.89 c.c.), proving the first precipitate to be manganese dioxide.

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[1] Hittorf and Salkowsky, *Zeitschr. f. Phys. Ch.*, XXVIII, 546–55 (1899).

[2] See Stieglitz, *Qualitative Analysis*, Part I, 269 ff.

The equation for the precipitation may be written as follows:

$$2AuCl_3+3MnCl_2+12KOH=2Au+3MnO_2+6H_2O+12KCl,$$

or, ionically: ?

$$2Au^{+++}+3Mn^{++}=2Au^{+}+3Mn^{++++}$$

It is evident from the preceding experiments that the precipitation may start before all the acid is neutralized, depending on the concentration of gold and manganous salt in the solution. Consequently substances which can partially neutralize the acid ought to induce precipitation. To test this conclusion a mixture of gold and manganous chlorides[2] in solution was made up as before, and small crystals of calcite were added. After 3 days the crystals were entirely coated with a brown precipitate of manganese dioxide (hydrated) and particles of gold were distinctly visible on close inspection. The equation may be written:

$$2AuCl_3+3MnCl_2+6CaCO_3=2Au+3MnO_2+6CaCl_2+CO_2$$

b) *Manganese carbonate.*—In the similar way it was shown that rhodochrosite can cause the precipitation of gold. In this case the reaction doubtless involved an additional stage, as follows:

$$MnCO_3+2HCl=MnCl_2+CO_2+H_2O,$$

after which the reaction was analogous to the one obtained with calcite, with the substitution of $MnCO_3$ for $CaCO_3$. In both cases carbon dioxide was evolved in noticeable quantity. Doubtless manganiferous calcite can react similarly.

It must be admitted that the concentration of gold and manganous salts used in these experiments were greatly in excess of any reported mine waters, but higher concentrations were necessary in outlining the nature of the chemical reactions involved. It remains to be shown that similar reactions can take place in extremely dilute solutions. Accordingly a liter of N/500 manganous chloride solution was made up and 38 mg. of gold in the form of chloride was added. Very dilute potassium hydroxide solution was added in small amounts, with repeated shaking until the solution was almost neutral to litmus. Precipitation occurred at once. The precipitate was allowed to settle for 24 hours, then all but 100 c.c. was decanted by means of a slow siphon. The remaining solution was filtered and added to the decanted portion. A 50 c.c. portion was tested for gold by the phenyl hydrazine test[1] in a Nessler tube, with blank for comparison. As this showed no gold, 500 c.c. of the solution was concentrated to 100 c.c. and the test was repeated. This again gave negative results. The test used readily detects concentrations of less than one part per million, consequently the second test showed the gold remaining in the original solution to be less than two parts in ten million. Since the precipitation is so complete we are forced to the conclusion that these reactions can take place in solutions of extreme dilution—such solutions as would be formed in the leaching of gold from a manganiferous lode.

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[1] Clowes and Coleman, *Quantitative Analysis*, p. 259.

[2] $MnCl_2$ was used instead of $MnSO_4$ to avoid the precipitation of gypsum.

The fact that in certain cases mine waters actually show alkaline reaction is well established. Emmons[2] has shown that at Ducktown, Tenn., the waters show decreasing acidity with depth. This was for water in an abandoned shaft. For circulating waters the change is probably greater. It is doubtless due to interaction with the constituent minerals of the surrounding rocks.

The following list gives the more common gangue and rock-forming minerals showing alkaline reaction to litmus or phenolphthalein:[3]

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[1] The phenyl hydrazine test mentioned has been described by Pozzi Escot, *Ann. de Ch. Anal.* (1907), XII, 90–91. It consists in adding to the solution to be tested, a few drops of formic acid, then a few drops of saturated phenyl hydrazine hydrochloride. The presence of gold is shown by a purple tint which may be used in the colormetric estimation of small amounts of gold. This method as tested by the writer gave strong tint in a 50 c.c. Nessler tube to solutions containing nine parts of gold in ten million of water. The advantage over the oxalic acid test is that the reaction is almost instantaneous and no heating is necessary.

[2] W. H. Emmons, *U.S. Geol. Survey Bull. No. 470*, p. 172.

[3] Kenngott, *Neues Jahrbuch* (1867), p. 302; F. Cornu, *Tschermak Mitteilung*, XXIV, 417–32, *a* XXV, 489.

Feldspars
Micas
Pyroxenes
Nephelite
Spodumene
Olivine
Serpentine
Talc
Tourmaline
Apatite
Calcite
Aragonite
Dolomite
Magnesite
Siderite
Vesuvianite
Noselite
Sodalite
Hauynite

It seems certain that if gold in solution escapes precipitation by sulphides, ferrous compounds, etc., and if gold and manganese-bearing solutions remain in contact with ordinary wall rock or gangue minerals for sufficient length of time, the acidity will be sufficiently reduced to allow the simultaneous precipitation of gold and manganese dioxide in the ore body.

It must be noted in this connection that the amount of manganese dioxide mixed with the gold is usually far in excess of that required by the equation given on p. 262.

Ferric salts, the most abundant oxidizing agents in mine waters, do not oxidize manganous salts to manganese dioxide, even in alkaline solutions. This was shown experimentally by making a solution of manganous sulphate and ferric sulphate, and slowly neutralizing the solution. Iron hydroxide was precipitated at once, but the manganese remained in solution until the solution became alkaline, when it was precipitated as manganous hydroxide.

Wells[1] has suggested an explanation for the precipitation of manganese oxides below the zone of acid waters, by the presence of small amounts of permanganates in the mine waters, which react with manganous salts to form manganese dioxide as follows:

$$2KMnO_4+3MnSO_4+2H_2O=5MnO_2+K_2SO_4+2H_2SO_4$$

The acid liberated is taken up by alkalies in case of an alkaline solution. This reaction has been used in the volumetric determination of manganese and is doubtless important if permanganates are present. No data available show permanganates in mine waters, and this theory needs verification before it is accepted as correct. However, it seems to be the nearest approach to an explanation of the precipitation of the excess of manganese dioxide over the stoichiometric proportion to gold, or the precipitation of the substance in any conspicuous amounts. The order of precipitation would, in general, depend on the concentrations of permanganate, gold chloride, and manganous salt, and the acidity of the solution; a complex relationship which has not as yet been worked out.

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[1] R. C. Wells, cited by Emmons, *Trans. Am. Inst. Min. Eng.*, XLII, 29 (1911).

V. OTHER INORGANIC SUBSTANCES

The number of inorganic substances capable of chemically precipitating gold, and occurring in ore deposits or mine waters, is doubtless rather large, but the more important ones only have been discussed.

Sulphur dioxide is used as a precipitant for gold, and either crystalline or colloidal gold may be formed by the action of this substance or sulphurous acid on solutions of gold chloride, the state of the gold depending upon conditions of temperature, concentration, etc.[1] Sulphur dioxide however is comparatively rare in mine waters, and probably may be neglected so far as precipitation of gold in an ore body is concerned. Similarly arsenious acid, and doubtless a great number of substance may be disregarded.

VI. ORGANIC COMPOUNDS

That a very great number of organic compounds can precipitate gold is very well known, and the idea that such precipitations occur in nature is by no means new. Rickard's experiments with the Rico shale[2] have been frequently referred to in the literature of ore deposits. Practically all organic compounds found in nature are reducing agents, and a very great number are strong enough to precipitate gold. Formic acid, oxalic acid, acetylene, glucose, and a host of others belong to the list.

Just what compounds are present in a carbonaceous shale, and just which of those present cause the precipitation, is at present impossible to say, but that many of them can cause precipitation seems unquestionable.

Amorphous carbon is capable of taking gold from gold chloride solution by absorption.[3] This seems to be a physical action rather than a chemical, but amorphous carbon may be present in carbonaceous shales and supposably might cause such precipitation. Whether other amorphous substances are capable of causing such precipitation has not been rigorously investigated.

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[1] See Gmelin-Kraut, *op. cit.*

[2] T. A. Rickard, *Trans. Am. Inst. Min. Eng.*, XXVI, 978 (1896).

[3] S. Brussow, *Zeitschr. Kolloid Chem. Ind.*, V, 137–38 (1909).

SUMMARY

If gold is in solution in waters circulating through an ore body many substances may cause precipitation of the gold. The ferrous compounds, derived from the partial oxidation of iron sulphides, are thought to be the most important, because they are formed comparatively readily from pyrite and other iron-bearing sulphides by the action of oxidizing waters,[1] they are very often, if not usually present in mine waters, and they are very effective precipitants for gold. The effect of the iron-bearing sulphides themselves cannot readily be separated from the action of ferrous salts, since in precipitating gold they may lead to the formation of ferrous sulphate, which, of course may cause farther precipitation of gold, if any is present. In most gold deposits sufficient pyrite, or other iron-bearing sulphide is present in the primary ore, to precipitate any gold that may be brought to the zone of sulphides. Less commonly siderite or iron-bearing calcite may be important. Siderite is attacked by acids more readily than pyrite, and consequently gives up ferrous salts more easily, and these, in solution, may cause the precipitation.

In comparatively rare cases, when the gold is in a solution containing manganous salts, contact with the country rock may neutralize the acids present and allow the manganous salt to reduce to gold. Rhodochrosite resembles siderite in its action except for the fact that no precipitation of gold can occur if the solutions are strongly acid, while in the case of siderite acidity does not inhibit the reduction of gold chloride to metallic gold.

The other reducing agents considered are thought to be of comparatively little importance, as they may be applied, to only a very few unusual deposits.

No attempt is made to explain the precipitation of gold from alkaline sulphide solutions, suggested by Lenher[1] as a possible means for the transportation of gold, as such solutions are not formed in the alteration of gold deposits. Their adequacy as a means for transportation and primary deposition of gold is beyond the scope of this paper.

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[1] Buehler and Gottschalk, *Econ. Geol.*, V, 28–35 (1910), and VII, 15–34 (1912).

In conclusion the writer wishes to express his thanks to Professor W. H. Emmons, who suggested this investigation, and to Professor Stieglitz, of the Department of Chemistry, for many helpful suggestions, on both theoretical considerations and practical experimental methods.

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[1] Lenher, *Econ. Geol.*, VIII, 744–50 (1912).

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